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1 **Solving multifunctionality in the carbon footprint assessment of primary metals production:**
2 **comparison of different approaches**

3

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8

9 **Abstract**

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Multifunctionality is a recurring issue in the life cycle assessment (LCA) of primary metals production, as one metal is often co-produced with other metals. In this context, this study aims at i) reviewing the approaches actually implemented in the literature for solving multifunctionality in the context of the LCA of primary metals co-production; ii) comparing the currently existing multifunctionality-solving approaches as defined by the ISO hierarchy, considering the carbon footprint assessment (in a life-cycle perspective) of copper (Cu), zinc (Zn), lead (Pb) and silver (Ag) co-production through the implementation of on-site “mine-to-metal” technologies at pilot scale in a Spanish mine; iii) discussing the implications associated with the use of these different approaches in the context of primary metals co-production and the extent to which they may affect the assessment of the environmental performances of metals. Overall, the allocation approach stands for the first option for solving multifunctionality in the LCA of metals co-production based on the review of 27 studies; despite the ISO hierarchy recommends the use of allocation as last resort. Based on a representative set of primary data drawn from on-site trials at a pilot scale, the potential climate change impacts induced by the co-production of 1 ton Cu and 6 tons Zn cathodes along with 2.65 tons Pb and 0.045 ton Ag precipitates are calculated to amount to 90,324 kg CO₂-eq in a life cycle perspective. Depending on the multifunctionality-solving approach, the apportionment of these impacts to each co-product shows significant discrepancies. The implementation of partial subdivision combined with market prices allocation attributes most (80%) of the impacts to Zn and Ag. The use of allocation approaches attribute the largest share of impacts to Zn (62%) and Pb (27%) when considering a mass criterion; while the impacts are primarily attributed to Ag (respectively 48% and 45%) and Zn (respectively 30% and 33%) when considering economic criteria (respectively market prices and production costs). In terms of representativeness, the use of partial subdivision shall be considered as a more representative approach for solving multifunctionality than the mere application of allocation. Moreover, the results obtained through the application of economic allocation are considered more consistent than those obtained by mass allocation in this case study; while the use of production costs may be seen as an alternative for overcoming the limits associated with market prices. Finally, the use of system expansion shows that the recovery of Zn, Pb and Ag in addition to Cu potentially avoids 25% of the total climate change impacts. The approach implemented to solve multifunctionality largely influences the estimated impacts of each co-produced metal, subsequently with potential large implications for the footprints of products and sectors using these metals. The way multifunctionality is solved shall therefore be transparently reported in the scope of LCA studies, with privileging subdivision whenever possible.

44 **Keywords**

45 Life cycle assessment; Multifunctionality; Allocation; Metals; Carbon footprint

46 1. Introduction

47

48 Essential to many everyday life applications, metals now play an important role within the modern
49 society. For decades, these materials faced increasing consumption trends, in particular due to a
50 growing worldwide population and rising technological standards. As example, the demand for metal
51 ores in the last decades was estimated to grow by 2.7% per year from 1970 to 2017 (UNEP
52 International Resource Panel, 2019). In the years to come, this demand for metals is expected to
53 maintain its exponential increase to satisfy an ever-growing market for manufactured goods. The
54 forecast from the OECD (2018), for instance, indicates a near three-fold rise of metals use over the
55 2011 - 2060 period (8 to 20 Gt).

56 Consequence of this rising metals demand, rich deposits tend to be depleted therefore leading to a
57 progressive ore grade decline, as e.g. in Australia where copper ore grade was shown to drop from
58 25% to 1-2% between 1840 and 2005 (Mudd, 2010). Given the situation, the ore grades are expected
59 to maintain their progressive decline in the future, e.g. in the case of copper whose ore grades are
60 foreseen to drop down to 0.1-0.2% by 2100 (Northey et al. 2014). Ores processing and metals
61 extraction are accordingly becoming more energy-intensive which, from an environmental
62 perspective, may translate into increasing environmental impacts (Norgate and Jahanshahi, 2010).
63 Moreover, ores are also becoming more complex in terms of mineralogy therefore requiring
64 additional efforts for accessing the valuable parts.

65 In this context, life cycle assessment (LCA) has widely been applied over the past few years for
66 assessing the environmental impacts associated with metals production; e.g. copper (Hong et al.,
67 2017a; Song et al., 2017; Memary et al., 2012), zinc (Qi et al., 2017; Van Genderen et al., 2016), lead
68 (Davidson et al., 2016), nickel (Mistry et al., 2016), gold (Chen et al., 2018), rare earths (Haque et al.,
69 2014; Vahidi and Zhao, 2018; Zaines et al., 2015). The implementation of LCA enables assessing a
70 product/process potential environmental burden, as functions of multiple impact categories, along
71 its entire life cycle (“cradle-to-grave”), i.e. from the raw materials extraction to the end-of-life
72 disposal. However, the application of LCA to the metals sector is not always straightforward, since
73 metal production processes often yield different co-products, which accordingly raises so-called
74 multifunctionality issues. From a methodological perspective, multifunctional systems represent an
75 issue regarding the apportionment of the environmental burden to each co-function/co-product
76 (Ekvall and Finnveden, 2001). To tackle this multifunctionality issue, the ISO standard 14044 (ISO,
77 2006) defines a three-step hierarchy (see Supporting Information document 1 for further details
78 about each approach):

79 1) Wherever possible, allocation should be avoided by:

- 80 • Subdivision, i.e. the multifunctional processes are to be divided into two or more sub-
81 processes for which data are individually collected;
- 82 • System expansion, i.e. the product system is to be expanded to include the additional
83 functions related to the co-products.
- 84 2) If allocation cannot be avoided, it should be first performed based on the underlying physical
85 relationships between the co-products/co-functions, i.e. the input and output flows relative to
86 the system under study are to be partitioned in a way that reflects how they are quantitatively
87 affected by quantitative changes in the products or functions provided by the system (e.g. mass).
- 88 3) If a clear physical relationship between the co-products cannot be established or used, the
89 allocation should then be performed based on other relationships (e.g. economic value).

90 In this context, this study firstly aims at discussing which approaches are actually implemented in the
91 literature to solve multifunctionality in the context of the LCA of primary metals co-production.
92 Secondly, considering as case study the co-production of copper, zinc, lead and silver in a Spanish
93 mine through the implementation of on-site “mine-to-metal” technologies including a
94 hydrometallurgical process, this study aims at comparing the different multifunctionality-solving
95 approaches as defined by the ISO standard. This case study is based on a representative set of data,
96 drawn from on-site trials at a pilot scale. Finally, the results are used to discuss the implications
97 associated with the use of these approaches in the context of primary metals co-production and the
98 extent to which they may affect the outcomes of the LCA.

99

100 **2. Literature review: multifunctionality issues in the LCA of primary metals co-production**

101

102 The literature review was performed using the Web of Science database (Clarivate, 2019), by
 103 applying a combination of keywords (screened in titles, abstracts and authors keywords) comprising,
 104 on the one hand, the terms “life cycle assessment” and “metals”, and on the other hand, terms
 105 relative to the “multifunctionality” issue and the approaches defined by the ISO standard (e.g.
 106 “subdivision”, “allocation”). Peer-reviewed research articles published after the year 2010 were
 107 privileged, with, however, the inclusion of three exceptions that were deemed relevant for this
 108 review: two articles published before 2010 respectively by Norgate et al. (2007) and Fthenakis et al.
 109 (2009), and one technical report published by the International Copper Association (2017). Based on
 110 the search results, 27 LCA studies mentioning multifunctionality issues in the context of primary
 111 metals co-production were eventually selected (Table 1).

112

113 *Table 1: Multifunctionality-solving approaches implemented in the literature, considering 27 LCA studies addressing primary*
 114 *metals co-production, sorted by year of publication*

Reference	Co-products considered in the product system	Multifunctionality-solving approaches implemented
Norgate et al., 2007	Lead (Pb), zinc (Zn), cadmium (Cd)	Mass allocation
Fthenakis et al., 2009	Zinc (Zn), indium (In), cadmium (Cd), germanium (Ge), gallium (Ga) Copper (Cu), molybdenum (Mo), selenium (Se), tellurium (Te)	Mass allocation; Economic allocation (Use of both approaches)
Northey et al., 2013	Copper (Cu), metallic by-products (<i>not specified</i>)	Economic allocation
Stamp et al., 2013	Platinum (Pt), rhodium (Rh), palladium (Pd), gold (Au), silver (Ag), indium (In), tellurium (Te), selenium (Se), copper (Cu)	Subdivision + economic allocation; Subdivision + mass allocation (Comparison of both allocation approaches)
Haque et al., 2014	Rare earths (RE)	Economic allocation
Molinare, 2014	Copper (Cu), molybdenum (Mo)	Full allocation to main metal (copper)
Nuss and Eckelman, 2014	63 metals	Economic allocation (Mass allocation as sensitivity analysis)
Kulczycka et al., 2015	Copper (Cu), lead (Pb), sulfuric acid	System expansion (substitution of lead and sulfuric acid)
Valero et al., 2015	Copper (Cu), molybdenum (Mo), silver (Ag), tellurium (Te) Nickel (Ni), copper (Cu), cobalt (Co)	Exergy allocation; Mass allocation; Economic allocation (Comparison of the three approaches)
Zaimes et al., 2015	Rare earths (RE)	Mass allocation (Economic and exergy)

		<i>allocations as sensitivity analysis)</i>
Davidson et al., 2016	Copper (Cu), zinc (Zn), silver (Ag), lead (Pb)	Mass allocation
Greig and Carey, 2016	Molybdenum (Mo), copper (Cu)	Mass allocation
Mistry et al., 2016	Nickel (Ni), platinum group metals, cobalt (Co), copper (Cu), iron (Fe), sulfuric acid	Economic allocation + system expansion (substitution of sulfuric acid)
Van Genderen et al., 2016	Zinc (Zn), lead (Pb), copper (Cu), lime, cadmium (Cd), cobalt (Co), manganese (Mn), aluminium (Al), sulfuric acid	Mass allocation + system expansion (substitution of sulfuric acid)
Westfall et al., 2016	Manganese (Mn), slag	Mass allocation
Hong et al., 2017a	Copper (Cu), other products (not specified)	Mass allocation
International Copper Association, 2017	Sulfide ore, oxide ore	Mass allocation
	Copper (Cu), molybdenum (Mo)	Mass allocation
	Iron (Fe), lead (Pb)/tin (Sn) alloy, steam, sulfuric acid	System expansion
Qi et al., 2017	Copper (Cu), precious metals, nickel (Ni)	Economic allocation
Qi et al., 2017	Zinc (Zn), other products (not specified)	Mass allocation
Song et al., 2017	Copper (Cu), silver (Ag), gold (Au)	Economic allocation
Kuipers et al., 2018	Copper (Cu), molybdenum (Mo), silver (Ag), selenium (Se), tellurium (Te)	Economic allocation
Vahidi and Zhao, 2018	Rare earths (RE)	Economic allocation
Van der Voet et al., 2018	Different co-products (not specified)	Economic allocation
Chen et al., 2019	Copper (Cu), sulfuric acid	Economic allocation
Tao et al., 2019	Lead (Pb), zinc (Zn), sulfur	Economic allocation
Dong et al., 2020	Copper (Cu), molybdenum (Mo)	Economic allocation
Islam et al., 2020	Copper (Cu), silver (Ag), gold (Au)	Economic allocation; Mass allocation <i>(Use of both approaches)</i>
Jiang et al., 2020	Lithium (Li), sodium sulfate, solid wastes	Economic allocation

115

116 Overall, the allocation approach stands for the first multifunctionality-solving approach in the 27 LCA
 117 studies reviewed, as opposed to the ISO hierarchy, which rather recommends the use of allocation as
 118 a last resort. Moreover, in most studies, the choice of the allocation approach does not appear to be
 119 justified, which accordingly does not enable capturing the rationale behind this methodological
 120 choice. In the case of primary metals co-production, the implementation of allocation primarily relies
 121 on three criteria (Figure 1):

- 122 ▪ Mass: this criterion is used for dealing with base metals (e.g. zinc; Qi et al., 2007) as well as
 123 precious metals (e.g. silver, gold; Davidson et al., 2016) or other special/rare metals (e.g. gallium,
 124 selenium; Fthenakis et al., 2009) co-productions.
- 125 ▪ Economic value: this criterion appears as the first option for dealing with precious (e.g. silver,
 126 gold; Song et al., 2017) and other special/rare metals (e.g. rare earths; Vahidi and Zhao, 2018). In

127 particular, the use of economic allocation primarily relies on market prices considering, in some
128 cases, averages over several years (e.g. Song et al., 2017; Mistry et al., 2016).

129 ▪ Exergy: this thermodynamic criterion is applied in two studies respectively for dealing with
130 base/precious metals (e.g. copper, silver; Valero et al., 2015) and rare earths (Zaimes et al., 2015).

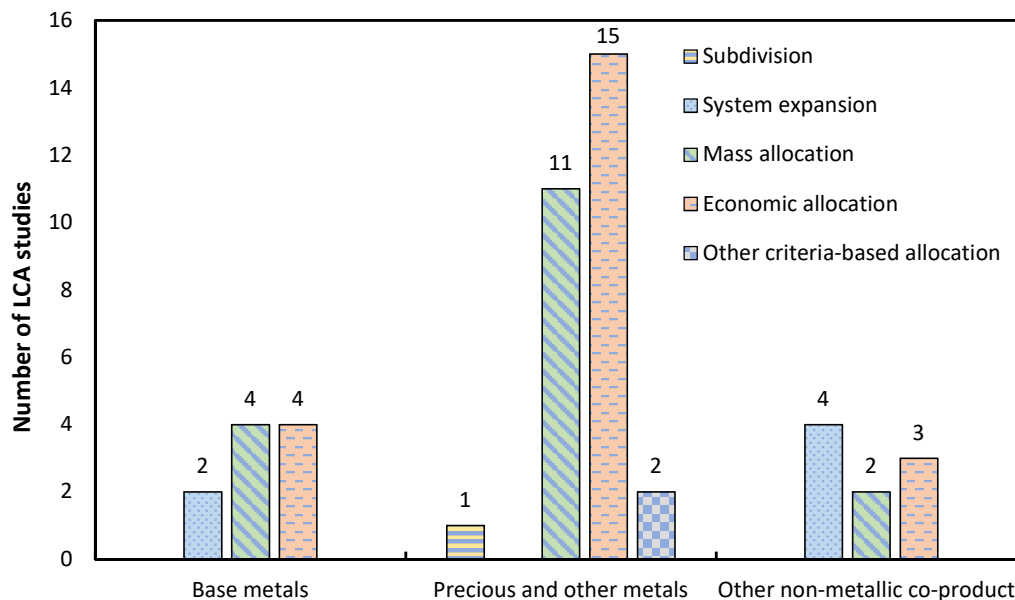
131 It is noteworthy that some of the reviewed studies distinctly use several allocation criteria for
132 information (Fthenakis et al., 2009; Islam et al., 2020), sensitivity analysis (Nuss and Eckelman, 2014;
133 Zaimes et al., 2015) or comparison and discussion purposes (Stamp et al., 2013; Valero et al., 2015).
134 Among these studies, Stamp et al. (2013) and Valero et al. (2015) in particular attempt to provide
135 recommendations as to the use of allocation approaches. While Stamp et al. (2013) compared the
136 use of economic and mass allocations, eventually concluding that none of the approaches clearly
137 stands out as the best option; Valero et al. (2015) compared exergy, mass and economic criteria,
138 eventually recommending the use of the exergy criterion, which may enable tackling some of the
139 limits relative to mass and economic allocations.

140 In contrast, the subdivision approach, defined as the first option in the ISO hierarchy (ISO, 2006), is
141 only applied in one of the 27 studies reviewed (Stamp et al., 2013). However, in this study, a full
142 subdivision of the system was not possible “for physical reasons”, which eventually led the authors to
143 combine subdivision with allocation for solving the multifunctionality issue. This overall limited use of
144 the subdivision approach may therefore partly be explained by its unfeasibility in some cases (e.g.
145 the consumption of energy in the comminution step is common to several minerals and associated
146 embodied metals, with no physical key that would enable dividing this consumption as functions of
147 the processed metals). Additionally, the significant data requirements for dividing processes into sub-
148 processes may represent another obstacle to the implementation of this approach (mining and
149 processing operations are often described using generic, averaged values or “black box models”;
150 Segura-Salazar et al., 2019). For example, Fthenakis et al. (2009) mentioned that their data were
151 “reported in aggregated forms”, which accordingly did not enable them to disaggregate the
152 production stages under study into different sub-processes.

153 Finally, the use of system expansion also appears relatively limited. In particular, system expansion is
154 primarily implemented for dealing with non-metallic co-products such as sulfuric acid, and in some
155 cases for dealing with base metals (Kulczycka et al., 2015; International Copper Association, 2017).
156 Hybrid approaches are also implemented by some authors, combining system expansion with other
157 approaches such as allocation. For example, Mistry et al. (2016) and Van Genderen et al. (2016)
158 combined system expansion for eliminating the not-required co-products (e.g. sulfuric acid) with
159 allocation for dealing with the co-products of interest.

160 Although the ISO standard considers the use of allocation as a last resort, one may consider this
161 approach appropriate in some situations. Indeed, besides the ISO hierarchy, the Joint Research

162 Center (JRC) of the European Commission (EC) provides guidelines in its ILCD¹ handbook (EC – JRC,
 163 2010) for solving multifunctionality depending on the decision-context. In particular, the use of
 164 allocation approaches may be justified in the case of attributional modelling (in a decision-context
 165 classified under situation C), when subdivision does not enable solving the multifunctionality issue.
 166 On another note, Santero and Hendry (2016) provide recommendations for solving multifunctionality
 167 specifically in the context of the LCA of metals production. While the use of system expansion is
 168 recommended as their first option, they justify the necessity of implementing allocation in some
 169 cases, as system expansion may not enable dealing with co-products that do not present any
 170 alternative mono-output production routes. In terms of criteria, the mass criterion is recommended
 171 for dealing with base metals whose economic values are relatively similar, while the economic
 172 criterion is recommended for dealing with precious metals whose economic values and production
 173 volumes are generally disproportional to those of other metals.
 174



175
 176 *Figure 1: Multifunctionality-solving approaches implemented in LCAs of primary metals production based on the review of*
 177 *27 studies, as functions of the types of co-products included in the product system²*
 178

179

¹ International reference Life Cycle Data system

² Base metals: Pb, Zn, Cu, Ni, Fe, Mn, Al, Sn

Precious and other metals: Cd, In, Ge, Ga, Mo, Se, Te, Pt, Rh, Pd, Au, Ag, RE, Co, Li

Other non-metallic co-products: sulfuric acid, lime, slag, steam, sulfur, sodium sulfate, solid wastes

180 3. Material and methods

181 3.1. Case study description

182 3.1.1. Goal and Scope definition

183

184 This case study focuses on a copper (Cu) open-pit mine located in Spain, in the Iberian Pyrite Belt.
185 The ore deposit comprises Cu sulphides as well as zinc (Zn), lead (Pb) and silver (Ag) minerals. The
186 mine site is equipped with “mine-to-metal” technologies enabling on-site ore mining/processing and
187 subsequent metals recovery through the implementation of a hydrometallurgical process.

188 The objective of this study is to compare multifunctionality-solving approaches in the carbon
189 footprint assessment of primary metals co-production (Cu, Zn, Pb and Ag) from a polymetallic ore.

190 Two different functional units are defined: on the one hand, a functional unit set as “the co-
191 production of 1 ton Cu cathode and 6 tons Zn cathode combined with the further recovery of 2.65
192 tons Pb and 0.045 ton Ag under precipitates forms” considering all co-products as targeted metals;
193 and on the other hand, a functional unit set as “the production of 1 ton Cu cathode” considering Cu
194 as the main targeted metal (given that the mine is first and foremost a copper mine) while other
195 metals are secondary.

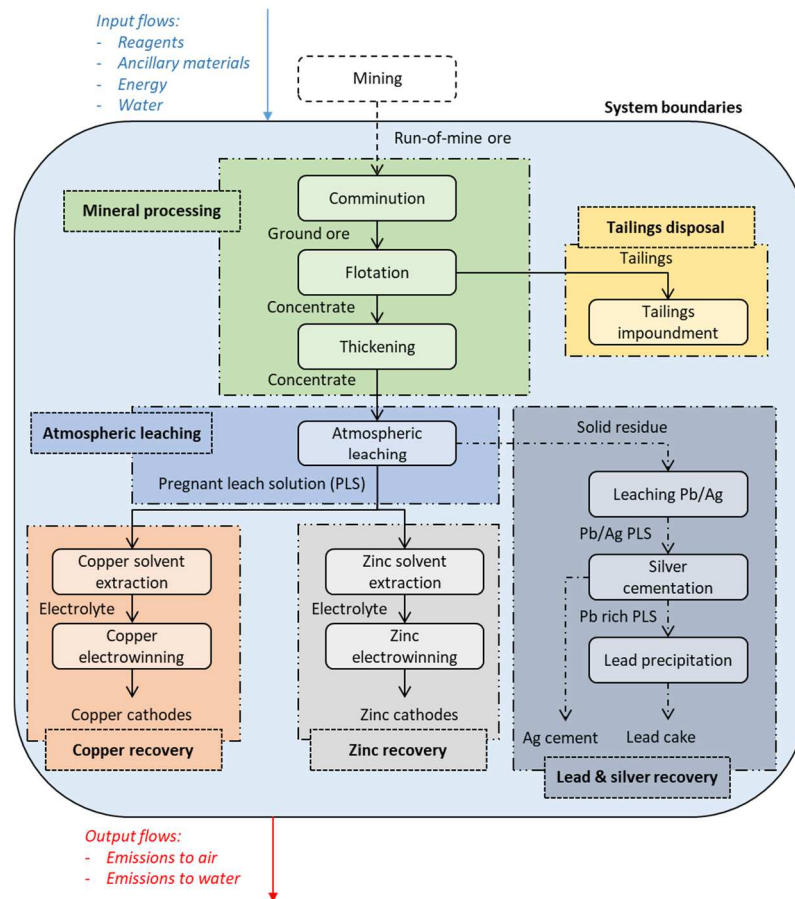
196 The system boundaries cover all the unit operations from the run-of-mine ore to the metals
197 recovered respectively under cathodes (Cu and Zn) and precipitates (Pb and Ag) forms, including i)
198 the production and supply of reagents, ancillary materials, energy and water; ii) the direct emissions
199 to the environment (Figure 2). The mining stage (encompassing drilling, blasting, loading/hauling
200 operations) is excluded from the system boundaries, in the absence of data specific to the mine
201 under study (“gate-to-gate” assessment). As stated in the ISO 14044 (2006), “the deletion of life cycle
202 stages, processes, inputs or outputs is only permitted if it does not significantly change the overall
203 conclusions of the study”. Given the goal of the study, it is assumed that the exclusion of the mining
204 stage from the system boundaries would not significantly affect the conclusions of this study, i.e. the
205 results from the comparison of different multifunctionality-solving approaches. It is however
206 noteworthy that the mining stage may have relatively large contributions to the environmental
207 impacts of the “cradle-to-gate” production of metals (e.g. regarding Cu mining and processing; Song
208 et al., 2017; Islam et al., 2020). Similarly, the construction of the mine and its infrastructure are also
209 disregarded in this study. The system boundaries thus encompass:

- 210 ▪ A mineral processing stage, through comminution, flotation and thickening, leading to the
211 production of a bulk concentrate containing Cu, Zn, Pb and Ag;
- 212 ▪ The management of tailings (impoundment) generated in the mineral processing stage;
- 213 ▪ An atmospheric leaching stage, producing, on the one hand, a pregnant leaching solution (PLS)
214 containing Cu and Zn; and on the other hand, a leaching residue containing Pb and Ag;

- 215 ▪ The recovery of Cu and Zn under cathodes forms, by solvent extraction and electrowinning;
- 216 ▪ The further recovery of Pb and Ag under precipitates forms from the leaching residue through
- 217 leaching and cementation/precipitation operations.

218 In line with the objective of this study, only one impact category is considered, namely climate
 219 change based on the IPCC 2007 (100 years timeframe) characterization model (IPCC, 2007). The life
 220 cycle impact assessment (LCIA) calculations are performed by use of the SimaPro v9 software.

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Figure 2: Process chain implemented on the mine site and considered system boundaries

225 3.1.2. Data inventory

226

227 The modelling of the foreground system (i.e. the processes for which specific data are used; Figure 2)
 228 relies on on-site data at pilot scale provided by the mining company. For confidentiality reasons, the
 229 data inventory is provided as elementary flows only (see Supporting Information document 2)
 230 derived from the data provided by the mining company by use of the Simapro software and
 231 ecoinvent v3.4 as the background database. The primary data encompass:

- 232 • Reagents and ancillary materials

233 Various reagents are consumed throughout this process chain, especially in the flotation (e.g.
234 collectors, frothers, Cu sulphate), leaching (e.g. sulfuric acid, flocculants, sodium chloride) and Zn SX-
235 EW (e.g. hydrochloric acid, sodium hydroxide, sodium sulfide) steps. The use of ancillary materials
236 primarily includes chrome and forged steel consumption in the comminution step, due to the
237 abrasion of the crushing/grinding equipment.

238 • Energy consumption

239 The energy consumption includes the use of electricity supplied by the Spanish grid throughout the
240 entire process chain, and the use of heat (steam) in the Zn SX and leaching of Pb/Ag steps.

241 • Water consumption

242 Water is consumed in different steps of the process (e.g. comminution, flotation, leaching) and is
243 supplied from the river (located near the mine site).

244 • Emissions to air

245 The emissions to air include direct emissions of dust due to comminution operations, of volatile
246 organic compounds (VOC) in the flotation and Zn SX steps, and of carbon dioxide (CO₂) in the Zn SX
247 step.

248 • Emissions to water

249 Contrarily to the other (above-presented) foreground data modelled by use of site-specific values,
250 emissions of metals to groundwater from sulfidic tailings disposal are calculated from the ecoinvent
251 model (Doka, 2008) as a proxy, considering on the one hand, the tailings composition provided by
252 the mining company and on the other hand, the transfer coefficients to groundwater as reported in
253 the Doka model. It is however to be noted that the uncertainty of these data is relatively important.

254 The background system, i.e. all the processes upstream and downstream the process chain under
255 study (for example, electricity generation or reagents production), is modelled by use of the
256 ecoinvent v3.4 database (Weidema et al., 2013).

257

258 3.2. Approaches implemented for solving multifunctionality

259

260 The system under study is a four-output system co-producing three base metals (1 ton Cu, 6 tons Zn,
261 2.65 tons Pb) and one precious metal (0.045 ton Ag). In accordance with the goal of the study, five
262 multifunctionality-solving approaches are considered: i) partial subdivision combined with economic
263 allocation based on market prices; ii) system expansion including substitution; iii) mass allocation; iv)
264 economic allocation based on market prices; v) economic allocation based on production costs.
265 Approaches i), iii), iv) and v) are implemented with respect to the first defined functional unit (the co-
266 production of the four metals) as they aim at apportioning the environmental burden to each co-

267 product, while approach ii) is implemented with respect to the second functional unit (focused on Cu
 268 production) as it aims at assessing the avoided burden potentially resulting from the co-products. It is
 269 to be noted that, while Cu and Zn are produced under refined metal forms (i.e. final products), Pb
 270 and Ag are produced under precipitate forms, which are in contrast intermediary products. In the
 271 absence of data regarding the downstream processing stages of Pb and Ag (i.e. from precipitates to
 272 refined metals), the different multifunctionality-solving approaches are here applied to these
 273 intermediary products.

274

275 3.2.1. Approach 1: partial subdivision and economic allocation based on market prices

276

277 In this case study, subdivision can be applied to the process chain by dividing the whole system into
 278 six different sub-systems as represented in Figure 2: mineral processing, tailings disposal,
 279 atmospheric leaching, Cu recovery, Zn recovery and Pb/Ag recovery. Cu recovery and Zn recovery are
 280 mono-functional sub-systems respectively recovering Cu and Zn. The other sub-systems, however,
 281 remain multifunctional as they process different metals simultaneously; therefore, the mere
 282 application of system subdivision in this case is not sufficient to solve the multifunctionality issue,
 283 which accordingly requires the implementation of another approach. In this respect, economic
 284 allocation based on market prices is combined with subdivision in order to deal with the
 285 multifunctional sub-systems, i.e. mineral processing, leaching and Pb/Ag recovery (Table 2).

286

287 *Table 2: Description of the different sub-systems and of the economic allocation factors considered in each multifunctional*
 288 *sub-system*

Sub-systems	Unit operations	Associated metals	Economic allocation factors (based on market prices ³)
Mineral processing	Comminution	Cu, Zn, Ag, Pb	Cu: 11.6 % Zn: 29.6 % Ag: 48.2 % Pb: 10.6 %
	Flotation		
	Thickening		
Tailings disposal	Tailings impoundment		
Atmospheric leaching	Atmospheric leaching		
Cu recovery	Cu solvent extraction	Cu	/
	Cu electrowinning		
Zn recovery	Zn solvent extraction	Zn	/
	Zn electrowinning		
Pb/Ag recovery	Pb/Ag leaching	Ag, Pb	Ag: 81.9 % Pb: 18.1 %
	Ag cementation	Ag	/
	Pb precipitation	Pb	/

289

³ Explained in sub-section 3.2.3

3.2.2. Approach 2: system expansion including substitution

The implementation of the system expansion including substitution approach implies that some functions provided by the system are considered secondary. In this case, Cu production is set as the main function (as defined in the second functional unit). Accordingly, Zn, Ag and Pb productions are considered as the co-functions to substitute. Metals co-products may be substituted, on the one hand, by the same metal produced from an alternative mono-output route (Santero and Hendry, 2016); or on the other hand, by a different material providing a similar service (Weidema and Norris, 2002).

In this respect, two alternative mono-output production routes were considered respectively for Zn and Pb, based on LCA case studies:

- The production of primary Zn through electrolysis, considering the whole process chain from ore mining to refined primary metal (Werder and Steinfeld, 2000).
- The production of primary Pb in China, considering the whole process chain from ore mining to refined primary metal (Hong et al., 2017b).

As for Ag, no alternative mono-output production routes were found, therefore as a second approach, the substitution was applied considering the service provided by the co-product. For this purpose, the main applications relative to Ag were first identified: electronics (23%), jewelry (20%) and coins/ingots (20%; BRGM, 2017). Based on these three applications, potential substitutions for Ag were identified considering alternative materials providing similar services than those provided by Ag. As example, Ag used in electronics may be substituted with Cu, aluminum (Al) or other precious metals; silver-made jewelry may be replaced with gold-made jewelry (U.S. Geological Survey, 2018; EC, 2017). Among these different substitution possibilities, only data regarding Al production were found to result from a mono-output production route. Accordingly, it is assumed in this study that Ag is substituted with Al, considering an end use in electronics and a hypothetical one for one substitution ratio (i.e. one ton Ag substituted with one ton Al). It is however to be noted that such an assumption is not fully representative of the reality, and therefore implies some uncertainty in the results. Data relative to Al production are drawn from the ecoinvent v3.4 database.

3.2.3. Allocation approaches

Three allocation approaches are considered in this case study, relying on three different criteria:

- The mass of each produced metal, as defined in the first functional unit;

323 • Worldwide market prices averaged over three years (2016 – 2018) drawn from the S&P Global
324 Market Intelligence database (2018);

325 • Worldwide metals production costs averaged over three years (2016 – 2018) drawn from the
326 S&P Global Market Intelligence database (2018). The description and rationale for the use of
327 these production costs can be found in the Supporting Information document 1.

328 From these criteria, different allocation factors (A.F) are calculated based on the following equations
329 (M.P = Market Prices; P.C = Production Costs), and subsequently used for partitioning the input and
330 output flows relative to the process chain to each output metal:

331

$$A.F_{mass} = MASS_{metal} \div \sum MASS_{metals} \quad (1)$$

332

$$A.F_{M.P} = (M.P_{metal} \times MASS_{metal}) \div \sum (M.P_{metals} \times MASS_{metals}) \quad (2)$$

333

$$A.F_{P.C} = (P.C_{metal} \times MASS_{metal}) \div \sum (P.C_{metals} \times MASS_{metals}) \quad (3)$$

334

335 In the absence of economic data relative to Pb and Ag under precipitate forms, the allocation is here
336 applied considering information about Pb and Ag under refined metal forms as proxy.

337

338 4. Results and discussion

339 4.1. Description of the results

340

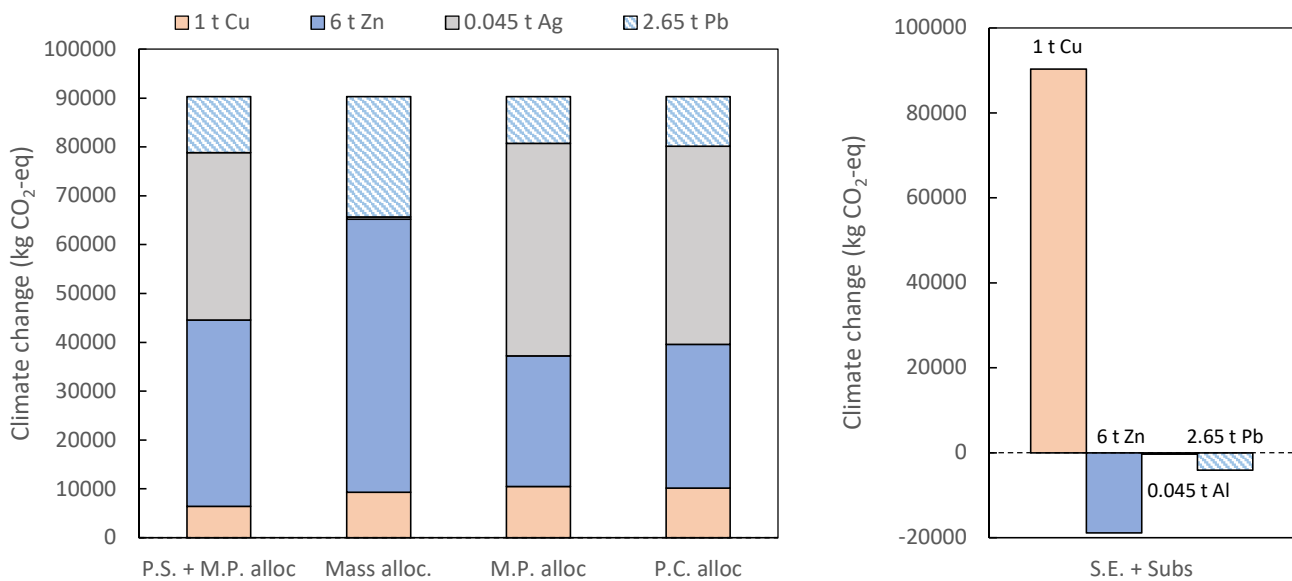
341 In a life-cycle perspective, the co-production of 1 ton Cu cathode and 6 tons Zn cathode, combined
342 with the further recovery of 2.65 tons Pb and 0.045 ton Ag under precipitates forms generates a total
343 of 90,324 kg CO₂-eq, considering the climate change impact category. In particular, these impacts are
344 primarily driven by i) the consumption of sodium hypochlorite as reagent in the Pb/Ag leaching step;
345 ii) the direct air emissions of carbon dioxide in the zinc solvent extraction step; and iii) the
346 consumption of electricity in different unit operations, especially in the zinc electrowinning step. The
347 detailed contributions analysis can be found in the Supporting Information document 1.

348 Depending on the multifunctionality-solving approach considered, the apportionment of these
349 impacts to each co-product shows relatively important discrepancies (Figure 3). It is noteworthy that
350 each multifunctionality approach does not affect the overall impacts induced by the process chain,
351 but only affects the share of impacts attributed to each co-product.

352 Firstly, the implementation of partial subdivision combined with market prices allocation leads to Zn
353 and Ag productions carrying the largest shares of the carbon footprint, respectively 42.2 and 37.9%
354 of the total impacts. In comparison, Pb and Cu productions carry relatively modest amounts of
355 impacts (respectively 12.7 and 7.1% of the impacts).

356 Secondly, the use of allocation approaches lead to different results depending on the considered
357 criterion. On the one hand, mass allocation attributes most of the carbon footprint to Zn production
358 (61.9% of the impacts) and, to a lower extent, Pb production (27.3% of the impacts) while Cu receives
359 a relatively limited share of the impacts (10.3%). In this approach, Ag production nearly receives no
360 impacts as its allocation factor only amounts to 0.5%. On the other hand, market prices-based and
361 production costs-based economic allocations both lead to relatively similar results, as they both
362 attribute most of the impacts to Ag production (respectively 48.2 and 44.9% of the impacts) and Zn
363 production (respectively 29.6 and 32.5% of the impacts). In this case, Cu and Pb productions carry
364 more limited impacts than Ag and Zn (10-11% of the impacts).

365 Finally, the use of system expansion including substitution first attributes the entirety of the impacts
366 to Cu according to the second functional unit (production of 1 ton Cu cathode). To these impacts are
367 then subtracted those of the substitutes, i.e. the impacts relative to the alternative primary
368 production routes of Zn and Pb as well as the primary production of Al. In this approach, the total
369 avoided impacts represent 25% of the total impacts attributed to Cu. In other words, the recovery of
370 Zn, Pb and Ag in addition to Cu allows avoiding 25% of climate change impacts in comparison with
371 alternative production routes of Zn and Pb as well as Al production. In particular, Zn is responsible for
372 the largest amount of avoided impacts as it contributes to 21 of the 25% avoided impacts.



374 *Figure 3: Apportionment of the climate change impacts to the different output metals as functions of the different defined*
 375 *approaches (left)/Impacts and avoided burden resulting from the different co-products (right) (P.S. = Partial Subdivision; M.P.*
 376 *= Market Prices; P.C. = Production Costs; Alloc. = Allocation; S.E. = System Expansion; Subs = Substitution)*

377

378 4.2. Implications associated with multifunctionality solving in the LCA of primary metals co-

379 production

380

381 The results obtained through this case study highlight that the different approaches provided by the
 382 ISO standard for tackling multifunctionality issues may yield relatively different results that may
 383 accordingly lead to different interpretations (Figure 3).

384 If the functional unit includes different co-products, the system subdivision approach shall be seen as
 385 the most representative way to apportion the environmental impacts to each co-product. Indeed,
 386 subdivision enables breaking down the multifunctional system into different mono-functional sub-
 387 systems, therefore allowing a direct association of the environmental impacts induced by the sub-
 388 system with its respective co-product(s). Results obtained through subdivision are more robust from
 389 those obtained through other approaches, as they reflect the impacts actually induced by the system
 390 under study without any potential distortion caused by external parameters (e.g. economic data). In
 391 this case study, the use of subdivision enabled separating the unit operations relative to Cu and Zn
 392 recovery from the overall process chain into two mono-functional sub-systems (Figure 2), whose
 393 impacts were accordingly directly attributed respectively to Cu and Zn (accounting for 40% of the
 394 total climate change impacts). However, in the context of the LCA of primary metals co-production,
 395 system subdivision sometimes only allows a partial solving of the multifunctionality issue given that
 396 some unit operations of metal production processes cannot be further separated into mono-

397 functional sub-systems. For example, the ore mining and processing operations (comminution,
398 flotation, thickening and leaching in this case study; Figure 2) deal with the ore as a whole (i.e.
399 encompassing all metals contained in the ore); therefore, they do not offer disaggregation
400 possibilities with respect to the metals that are eventually recovered. In this case, other methods (e.g.
401 allocation) are to be combined with subdivision in order to solve the multifunctionality issue.
402 Although partial subdivision does not enable solving multifunctionality, it may render the issue
403 smaller and potentially easier to solve. Moreover, it may lead to relatively more accurate results,
404 different from those obtained through the mere use of allocation.

405 Regarding the allocation approach, the results showed significant discrepancies between mass and
406 economic allocations. While allocation by mass attributed most of the impacts to Zn as well as Pb and
407 almost none to Ag, allocation by market prices and production costs conversely attributed most of
408 the impacts to Ag, which captures the major part of the economic value. On the one hand, one
409 possible interpretation resulting from the use of mass allocation implies that no effort is
410 implemented to recover Ag, as it appears to induce no impacts. This could be consistent with a case
411 where Pb and Zn drive the production while Ag is only a secondary product without any economic
412 interest. On the other hand, the application of market prices allocation implies that the impacts are
413 attributed according to the revenue that will eventually be generated from the produced metals.
414 Therefore, this approach implies that Ag production is one driver of the mining activity, due to its
415 significant economic value, which may be considered as a more consistent scenario than that of mass
416 allocation. In this case study, the mere application of allocation however does not appear relevant, as
417 a system subdivision is possible (e.g. the mere use of allocation also attributes the impacts relative to
418 the Cu recovery sub-system to Zn, Pb and Ag). Accordingly, the allocation approach should be
419 considered as a complement to subdivision when the latter approach is possible but not sufficient to
420 solve the multifunctionality issue. The sole application of allocation should rather be considered as a
421 last resort option when unavoidable (i.e. any subdivision of the system is impossible).

422 In comparison with market prices, production costs allocation yield relatively similar results. However,
423 in terms of reliability, one may consider the latter approach is more reliable than market prices
424 allocation. Indeed, while market prices are subject to a certain volatility that can affect the allocation
425 results, production costs are more stable (see Supporting Information document 1). Moreover, the
426 use of these costs as a basis for allocation may be considered more correlated to the actual
427 environmental impacts in the sense that they primarily depend on the actual amounts of inputs
428 necessary to the production of metals, which may be considered to reflect in a more representative
429 way the actual efforts implemented to produce the metal. Production costs may therefore represent
430 a relevant alternative to market prices depending on the context of the study (market prices may
431 remain more relevant in some contexts, e.g. temporarily explicit LCAs considering market changes).

432 If the functional unit solely includes one product, the system expansion including substitution
433 approach may be seen as a relevant option that enables eliminating from the product system the co-
434 products assumed secondary. In practice, this substitution approach aims at accounting for the
435 avoided burden resulting from the multifunctional system under study. In other terms, according to
436 this approach, the production of co-products in addition to the main metal potentially avoids the
437 need for alternative productions, hence the avoided burden. In this study, Zn, Pb and Ag co-
438 productions (in addition to Cu) were considered to avoid the need respectively for alternative
439 productions of Zn through electrolysis, of Pb through refining and of Al, assumed to substitute Ag
440 within electronics. However, one issue relative to this approach is its complexity in terms of
441 implementation, given that it sometimes requires many efforts for identifying consistent alternatives
442 to the co-products assumed secondary. In particular, one difficulty is to access realistic substitution
443 rates when replacing a metal with another material. In this study, it has been assumed a hypothetical
444 one for one ratio for Ag substitution, however in practice the use of a metal in a given application can
445 generally be substituted only up to a certain rate. Moreover, system expansion also requires the
446 collection of supplementary inventory data relative to the considered alternatives. In particular,
447 these data have to result from mono-functional systems; otherwise, one potential risk that could be
448 encountered with this approach could be to solve a multifunctionality issue with another one.

449

450 5. Conclusions

451

452 This study enabled addressing the issue of multifunctionality in the LCA of primary metals co-
453 production, in particular through a case study focusing on the carbon footprint of primary Cu, Zn, Pb
454 and Ag co-production.

455 While the ISO standard defines a hierarchy of approaches to solve this issue, the literature review
456 highlighted that this hierarchy is generally not followed in LCA studies related to primary metals co-
457 production, as the allocation approach overall stands for the preferred option, as opposed to the ISO
458 hierarchy (but partly in line with some of the recommendations from the ILCD Handbook in the case
459 of attributional modelling). In comparison, the implementation of the subdivision and system
460 expansion approaches appears very limited in the reviewed studies.

461 Based on primary on-site data at pilot scale provided by the mining company, the climate change
462 impacts induced by the co-production of 1 ton Cu cathode and 6 tons Zn cathode along with the
463 further recovery of 2.65 tons Pb and 0.045 ton of Ag under precipitate forms were calculated to
464 amount to 90,324 kg CO₂-eq in a life-cycle perspective. Five multifunctionality-solving approaches
465 were applied to this case study so as to apportion these impacts to the different co-products, based
466 on the currently existing approaches defined by the ISO standard. The results highlighted significant
467 discrepancies depending on the considered approach. The implementation of partial subdivision
468 combined with market prices allocation leads to the apportionment of most impacts to Zn as well as
469 Ag. The mere application of allocation attributes most of the impacts to Zn as well as Pb and none to
470 Ag when applying a mass criterion; while the impacts are primarily attributed to Ag and Zn when
471 applying economic criteria (market prices or production costs). In terms of representativeness, the
472 use of partial subdivision enables a more representative apportionment of the impacts to the
473 different co-products as compared to the mere application of allocation. Moreover, in this case, the
474 use of economic allocation appears to lead to more consistent results than those obtained by use of
475 mass allocation; while the use of production costs for the economic allocation may be considered
476 more reliable given the limits associated with market prices. On the other hand, the use of system
477 expansion shows that the recovery of Zn, Pb and Ag in addition to Cu potentially avoids 25% of the
478 total climate change impacts in comparison with alternative production routes of Zn and Pb as well
479 as Al production (assumed to substitute Ag within electronics).

480 The discrepancy observed in these results emphasizes the need for carefully selecting the
481 multifunctionality-solving approach as it may significantly affect the outcomes of the LCA of primary
482 metals production. One may consider, despite the ISO hierarchy, that the choice of the appropriate
483 multifunctionality-solving approach, in practice, depends on multiple factors: the type of study
484 (attributional or consequential LCA), the availability of data (e.g. subdivision requires more detailed

485 data), the type of co-products, the methodological feasibility (e.g. subdivision is not applicable to all
486 operations of the metal production chain), etc. It is therefore necessary to justify the selected
487 approach and perform sensitivity analysis when solving multifunctionality (especially in decision-
488 support contexts), as it may subsequently result in important implications on the environmental
489 performance of products or sectors requiring metals.

490 In addition to the different multifunctionality-solving approaches compared in this study, other
491 approaches such as exergy-based allocation were recently developed but not included in this study.

492 In this regard, future works should focus on integrating these approaches to the comparison
493 performed in this study, so as to develop a comprehensive overview of the implications associated
494 with each existing multifunctionality-solving approach in the context of the LCA of primary metals co-
495 production.

496

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498

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